

SOME STUDIES ON THE PLATING OF COBALT AND  
NICKEL FROM COORDINATION COMPOUNDS

BY  
MARGARET DAVIS KRAMER

A. B., Meredith College, 1937  
M. S., University of North Carolina, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
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# SOME STUDIES ON THE PLATING OF COBALT AND NICKEL FROM COORDINATION COMPOUNDS

## INTRODUCTION

Coordination compounds have long been used in electroplating baths because experience has shown that such complexes are effective in producing smooth plates.

The constituents of electroplating baths have been chosen largely by trial and error, and not as the result of systematic studies of complexes. Recently, however, at least one author has stressed the study of cyano complexes as examples of Werner complexes (1).

In addition to their use as sources of metal ions, coordination compounds have been thought by some to be the key to the effectiveness of addition agents (2). Such an hypothesis of the nature of addition agents has not been subjected to systematic study.

There is little variety in the types of complexes used in industry for plating. The major use of coordination compounds to date has been the use of cyano complexes in the plating of copper, zinc, cadmium, gold, silver, and brass. Perhaps the lack of a study of electroplating agents as examples of Werner complexes has retarded the development of other types of baths.

The study reported in this thesis was undertaken in an attempt to determine whether some property or properties of a complex were important in characterizing the plating ability of that complex.

A variety of stable cobaltic ammines is available for a study such as this. Later some of the few stable cobaltous ammines were used.

Since nickel ammines are also generally stable in solution,

and since nickel electroplating, unlike cobalt electroplating, is important commercially, nickel amines were chosen for additional investigations.

### EXPERIMENTAL

Many of the compounds of cobalt studied were available from laboratory stock; others were made according to methods found in the literature. All of the nickel amines studied were prepared by methods outlined in the literature.

Preliminary plating tests were run on the cobalt complexes, using 0.5% solutions, platinum anodes, and varying current densities. Tests on the nickel complexes were done in the same fashion, but using 1% solutions and nickel anodes.

As a result of these plating tests, the complexes were classified according to their plating ability as good, fair, or poor. Examples of each type follow.<sup>1</sup>

Good:  $[\text{Coen}_3]\text{Cl}_3$ ,  $[\text{Nien}_3]\text{Cl}_2$

Fair:  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2\text{SO}_4$ ,  $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ ,  $[\text{Nipn}_3]\text{Cl}_2$ ,  
 $[\text{Nihn}_3]\text{Cl}_2$

Poor:  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Copen}_4\text{Cl}_2]\text{Cl}$ ,  $[\text{Nipy}_4]\text{Cl}_2$ ,  
 $[\text{Ni}(\text{stien})_2]\text{Cl}_2$ ,

and all of the ammonia derivatives containing nitro groups which were tried.

The change of pH during plating was studied, using 0.5% solutions and a current of 0.2 ampere for 20 minutes. The change in pH is apparently not an important factor in producing good plates, for complexes producing good plates showed the same sort of pH changes as those producing poor ones. Fluoborate was found to be an excellent buffer for nickel plating baths.

Current efficiency studies were made on many of the baths. In the case of  $[\text{Coen}_3]\text{Cl}_3$ , it was found that cobalt plates from the trivalent state, but dissolves from the anode in the divalent condition. We were not able to find a co-

<sup>1</sup>Abbreviations used are: en, ethylenediamine; pn, propylenediamine; bn, butylenediamine; py, pyridine; stien, stilbenediamine.



ordinating agent which would allow the cobalt to dissolve from the anode in the trivalent state. There is evidence that  $[\text{Coen}_3]\text{Cl}_3$  is regenerated in the bath, the  $[\text{Coen}_3]^{++}$  ion which is probably first formed being oxidized by air to  $[\text{Coen}_3]^{+++}$ .

A bath containing  $[\text{Nien}_3]^{++}$  and some excess ethylenediamine gave cathode efficiencies of 90% or above. This bath is being studied further.

### DISCUSSION

The data collected during this study indicate definitely the effect of stability of the complex and the effect of steric hindrance offered by the coordinating amine to the metal ion during plating. It has been found that an ammine of intermediate stability toward reduction is better for producing a plate than a very stable one or a very unstable one. It has also been found that large organic groups can so shield a metal ion that the plate produced is progressively poorer as the size of the substituent group increases.

Using half-wave potentials (3,4) as a measure of stability toward reduction, it is found that complexes with potentials more negative than about  $-0.75$  v are poor or non-plating agents; complexes with half-wave potential between  $-0.70$  v and  $-0.50$  v are generally good plating agents; while those with half-wave potential less negative than  $-0.50$  v are poor plating agents. In each case, the exceptions to this generalization are ethylenediamine complexes. This leads to the supposition that stability is not the only factor.

As a result of studying a series of substituted ethylenediamines as complexing agents, it was found that the size of the coordinating group is important. The effect of stability cannot be neglected here, however, for stability usually decreases with increasing molecular weight of the amine. Moreover, the diamines can achieve stability through chelation, whereas a coordinating group like pyridine cannot.

The progressively poorer plating character as the size of the substituent group increases is partially a steric effect.

Substituent groups actually serve to hinder plating of the metal ion.

Further data are needed to establish the bounds of stability and the limits of substitution more exactly.

The actual mechanism by which a complex accepts electrons becomes important, for if the metal plates directly from the complex rather than from the aquated ion, some of the coordinating amine might be included in the plate. This inclusion may account for the non-adherence of some of the plates. We have been able to detect nitrogen in plates from a cobaltic pyridine complex and from the hexammino cobaltic ion, but we have not found it in the plates from a cobalt-ethylenediamine bath. These data are too incomplete to permit drawing any conclusions.

#### SUMMARY

1. A series of cobaltic ammines and one of nickelous ammines, together with a few cobaltous ammines, have been studied from the point of view of their function as electroplating agents.

2. It is suggested on the basis of the data collected that stability of complex ions and character of the coordinating group are decisive factors.

3. The ability of coordination compounds containing substituted ethylenediamines to produce good plates decreases with increasing size of the coordinating group.

4. Stability of the complex ion is an important factor for the ammonia derivatives and for the ethylenediamine derivatives. A compound may be too stable toward reduction or too unstable to plate satisfactorily.

5. Within the limits of the data collected, we have not been able to demonstrate that pH is an important factor in the formation of a good plate.

6. Fluoborate has been found to be superior to pyrophosphate as a buffer in the nickel plating baths of the type used in this study.



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## VITA

The author was born in Elizabeth City, N. C., October 19, 1915. She attended the public schools of that city, graduating from the Elizabeth City High School in 1933. She received her A. B. degree from Meredith College, Raleigh, N. C., in 1937, with a major in chemistry. She holds the degree of Master of Science in Chemistry from the University of North Carolina, Raleigh, N. C., conferred in 1940. She has been teaching in the Department of Chemistry of Meredith College since 1938, and is at present on leave from that institution.

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